Chemical decoration in cubic approximant and quasicrystal in the Al-Cu-Fe system

Journal:	*Philosophical Magazine & Philosophical Magazine Letters*
Manuscript ID:	TPHM-05-May-0170.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	19-Jul-2005
Complete List of Authors:	Simonet, Virginie; Laboratoire L. Néel, CNRS HIPPERT, Francoise; Laboratoire des Materiaux et du Genie Physique, ENSPG BRAND, Richard; Universität Duisburg-Essen, Department of Physics CALVAYRAC, Yvonne; CECM, CNRS RODRIGUEZ-CARVAJAL, Juan; Laboratoire Léon Brillouin, CEA - CNRS Sadoc, Anne; Université de Cergy Pontoise, LPMS
Keywords:	X-ray diffraction, structure analysis, quasicrystals, EXAFS
Keywords (user supplied):	local order

Chemical decoration in cubic approximant and quasicrystal in the Al-Cu-Fe system

V.SIMONET[1], F. HIPPERT[2*], R.A. BRAND[3], Y. CALVAYRAC[4],

J. RODRIGUEZ-CARVAJAL[5] and A. SADOC[6]

[1] Laboratoire Louis Néel, CNRS, BP 166, F-38042 Grenoble Cedex 9, France

[2] LMGP, ENSPG, BP 46, F-38402 Saint Martin d'Hères Cedex, France

[3] Department of Physics, Universität Duisburg-Essen, D-47048 Duisburg, Germany

[4] CECM/CNRS, 15 rue G. Urbain, F-94407 Vitry-sur-Seine Cedex, France

[5] Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay, F-91191 Gif sur Yvette Cedex, France

[6] LPMS, Université de Cergy-Pontoise, F-95031 Neuville sur Oise Cedex, France

Abstract

The local order in the Al-Cu-Fe quasicrystal and in two of its approximants has been investigated by extended X-ray absorption fine structure (EXAFS) studies at the Cu and Fe K-edges. The chemical occupation of the crystallographic sites in the 1/1 cubic α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ phase is revisited. From these results, a model for the chemical short-range order in the $Al_{62}Cu_{25.5}Fe_{12.5}$ quasicrystal is proposed.

Keywords: quasicrystals, EXAFS,X-ray diffraction, structure analysis, local order

1 Introduction

An accurate description of the atomic positions in quasicrystals (QC) is available [1, 2] but their occupation by the different chemical species is still not completely solved. This is an important question because the chemical local order, especially the Al-transition metal bonds, plays a central role in determining the atypical electronic properties of QCs and probably their stability through the pseudo-gap formation. A way to obtain information on the local order in QCs is provided by the existence of approximants. With increasing integers p and q which characterize the approximant order, the size of the unit cell increases and the local structure approaches that of the parent QC on an increasing scale. In the Al-Cu-Fe system, several high order approximants (p/q = 3/2, 4/3 …) exist for compositions similar to those of the quasicrystal (around $Al_{62}Cu_{25.5}Fe_{12.5}$) [3]. Besides, a cubic 1/1 phase, hereafter denoted as α, can be stabilized by the substitution of a few percent of Si for Al, in a small domain around $Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ [4,5]. The Al(Si)-Cu-Fe system offers therefore the opportunity to study experimentally the evolution of the local order from the relatively simple cubic 1/1 phase to complex approximants and finally to the quasicrystal. For this purpose EXAFS studies have been performed at the Cu and Fe K-edges in the cubic α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and in the QC-$Al_{62}Cu_{25.5}Fe_{12.5}$ and at the Cu K-edge in rhombohedral and QC phases with exactly the same composition $Al_{62.8}Cu_{26}Fe_{11.2}$.

The structure of the rhombohedral phase is still unknown. For the α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ phase, two slightly different structural models have been proposed from X-ray diffraction [6, 7]. The occupied crystallographic positions are almost identical but the chemical occupation differs significantly. Besides, none of these models was found able to explain the present EXAFS data. This led us to revisit the structure of the α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ phase by combining X-ray and neutron powder diffraction and EXAFS analysis [5]. The obtained

chemical decoration is presented in Table 1, using a cluster description. The atomic structure of the α-phase can be described by introducing two Mackay clusters located at (0,0,0) and (1/2,1/2,1/2) respectively. Following Ref. [8], the remaining atoms are included on additional shells around the Mackay cluster located at (0, 0, 0).

2 Experiments

Ribbons made by planar flow casting were annealed under high vacuum: 24 hours at 650°C for α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$, 72 hours at 705 °C for $Al_{62.8}Cu_{26}Fe_{11.2}$ in its rhombohedral state and 2 hours at 740°C in its QC state, and 2 hours at 800°C for the QC-$Al_{62}Cu_{25.5}Fe_{12.5}$. Compositions are the nominal ones. No foreign phase was detected within the accuracy of X-ray powder diffraction. Ribbons were ground into a fine powder for the EXAFS experiments which were performed on the D42 beamline of the DCI storage ring at LURE (Orsay, France) in the transmission mode at the Fe K-edge (7112 eV) and at the Cu K-edge (8979 eV) at 15 K. The extraction and analysis of the EXAFS oscillations were performed using the FEFF package [5, 9]. The Fourier transform (FT) of the $k^2\chi(k)$ signal was calculated in the k-range [3.4 - 12 $Å^{-1}$] by using a Hanning window. Fits were performed in restricted r-ranges ([1.7 – 3 Å] at the Fe K-edge and [1.3 - 3.1 Å] at the Cu K-edge).

3 Results

The modulus and imaginary part of the FT of the measured EXAFS oscillations $k^2\chi(k)$ are reported in Figures 1 and 2. At the Cu K-edge, a very small composition effect is detected when comparing the two QCs but the FT of the rhombohedral approximant and the QC of same composition, $Al_{62.8}Cu_{26}Fe_{11.2}$, are identical up to 6 Å, which reveals identical local

environments around Cu in this range (Fig. 1). Although the FTs of the QC-$Al_{62}Cu_{25.5}Fe_{12.5}$ and α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ phases are quite similar, significant evolutions are observed especially around Cu and to a lesser extent around Fe (Fig.2).

3.1 Local order in the cubic approximant α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$

Fe and Cu spectra were fitted simultaneously. All possible single scattering paths in the fitted r-range around a given absorbing atom were considered (more than 50 at the Cu K-edge). No distinction was made between Al and Si. The structural model obtained from the analysis of X-ray and neutron powder diffraction data (Table 1) has been used as a starting point. The distances between the absorbing atom and its neighbours were allowed to vary but the same relative variation δr/r was imposed for all similar pairs, i.e. involving the same kind of atoms, in order to limit the number of parameters. The relative mean displacement σ^2 of a pair (Debye-Waller factor) was refined but held equal for all similar pairs. In order to further improve the fit, the chemical nature of atoms on sites (3), (4), (5), (6), (10) occupied by a mixture of different species, was allowed to vary, the stoichiometry being held fixed. Only small changes from the initial model are necessary to converge to the very good fits shown in Figure 2. In particular, the coexistence of Al, Cu and Fe on site (5) is confirmed by the EXAFS analysis. It is interesting to describe the results by analysing the average environment of Cu or Fe (Table 2). One of the most striking results is that Fe has no Fe first neighbours and is surrounded mainly by Al atoms and a small proportion of Cu. The calculated summed contributions of all neighbours of the same kind around a given absorbing atom are drawn in Figure 2, which demonstrates that the double peak in the FT at the Cu K-edge originates from destructive interference between the Al and Cu contributions.

3.2 Local order in the quasicrystal QC-$Al_{62}Cu_{25.5}Fe_{12.5}$

A fit of the EXAFS spectra of the QC was attempted, starting from the results of the EXAFS analysis in the α-phase and using the same fit procedure. In addition, the possibility of adding a Fe atom at the (1/2,1/2,1/2) position was tested. Results are presented in Tables 1 and 2 and in Figure 2. All pair distances in the QC are slightly smaller than in the α-phase and the average number of neighbours changes slightly (Table 2). As a main result, in the QC, the Cu atoms in site (5) are totally replaced by Al and occupy site (6) instead. The fits are slightly better with both centres of the Mackay clusters filled with one Fe atom. These results show that the local order in the QC up to 3 Å can be accounted for by introducing only small variations in the model of the α-phase. This confirms the structural and chemical closeness of both phases. However, the details of the proposed structure and its description in terms of icosahedral clusters must be confirmed by other methods since EXAFS alone cannot solve complex structures.

4 Conclusion

From a complex EXAFS analysis, associated to joined X-ray and neutron diffraction, we have been able to determine the chemical decoration in the cubic 1/1 α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ approximant. Fe atoms are found in the outer icosahedra of the two MacKay clusters (sites (5) and (9)). This is similar to the case of Ru in the 1/1 Al(Si)-Cu-Ru [10] or Mn in the 1/1 Al(Si)-Mn approximants [8]. The existence of a composition domain for the cubic α-Al(Si)-Cu-Fe results mainly from the variations of the Fe, Al and Cu occupations on site (5) keeping site (9) entirely filled by Fe [5]. The results on the cubic α-phase have then been used

to propose a chemical decoration in the quasicrystal, pointing out the similarity in the local order in the two phases on a scale at least up to 3 Å. An important conclusion of the present work is that an analysis of all scattering paths is mandatory to interpret the EXAFS oscillations in complex phases. Grouping neighbours into shells with a Gaussian distribution of distances, as done in previous EXAFS analysis of approximants and quasicrystals, leads to erroneous results, in particular to artificially low coordination numbers, because it does not take into account destructive interferences between individual scattering paths and because the assumption of a Gaussian distribution is not valid.

References

[1] D. Gratias, F. Puyraimond, M. Quiquandon and A. Katz, Phys. Rev. B **63** 24202 (2000).

[2] A.Yamamoto, H. Takakura and A. P. Tsai, Phys. Rev. B **68** 094201 (2003).

[3] M. Quiquandon, A. Quivy, J. Devaud et al , J. of Physics: Condens. Matter **8** 2487 (1996)

[4] A. Quivy, M. Quiquandon, Y. Calvayrac et al, J. of Physics: Condens. Matter **8** 4223 (1996).

[5] V. Simonet, F. Hippert, R.A. Brand et al, accepted for publication in Phys. Rev. B

[6] Z.-M. Stadnik, T. Takeuchi, N. Tanaka and U. Mizutani, J. of Physics: Condens. Matter **15** 6365 (2003).

[7] F. Puyraimond, M. Quiquandon, D. Gratias et al, Acta Cryst. A **58** 391 (2002).

[8] K. Sugiyama, N. Kaji and K. Hiraga, Acta Cryst. C **54** 445 (1998).

[9] J. J. Rehr and A. L. Ankudinov, J. Synchrotron Rad. **8** 61 (2001) and refs therein.

[10] T. Takeuchi and U. Mizutani, J. of Alloys and Compounds **342** 416 (2002).

Cluster at (0,0,0)									Cluster at (1/2,1/2,1/2)				
shell	centre	ico	icosi		ico	rhombico		ico	centre	ico	icosi		ico
Site	(1) 1a	(2) 12j	(3) 24l	(4) 6e	(5) 12j	(11) 12j	(12) 12k	(10) 6f	1b	(6) 12k	(7) 24l	(8) 6h	(9) 12k
α diffrac.	Fe 1	2.414 Al 10.1	4. 537 Cu/Al 16.8/7.2	4.627 Cu/Al 3.8/2.2	4.690 Cu/Al/Fe 5.6/2.4/4	6.349 Al 12	6.505 Al 12	7.276 Cu/Al 5.6/0.4	empty	2.415 Al/Cu 9.2/2.8	4.670 Al 24	4.732 Al 6	4.653 Fe 12
α EXAFS	Fe 1	Al 10.1	Cu/Al 15.2/8.8	Cu/Al 6	Cu/Al/Fe 5.2/2.8/4	Al 12	Al 12	Cu 6	empty	Al/Cu 9.8/2.1	Al 24	Al 6	Fe 12
QC EXAFS	Fe 1	Al 10.1	Cu/Al 15.4/8.6	Cu 6	Al/Fe 9/3	Al 12	Al 12	Cu 6	Fe 1	Al/Cu 3.8/8.2	Al 24	Al 6	Fe 12

Table 1: Chemical decoration of the icosahedral clusters in the α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and QC-$Al_{62}Cu_{25.5}Fe_{12.5}$ phases. Shell labels "ico", "icosi" and "rhombico" stand for icosahedron, icosidodecahedron and rhombicosidodecahedron respectively. For the α-phase, results from X-ray and neutron powder diffraction [5] are reported. The nature and number of the atoms on each crystallographic site (numbered as in Refs. [5, 7]) and their distance from the cluster centre are given. The chemical decoration deduced from the EXAFS analysis is reported for the α and QC phases.

Sample edge	Al neighbours	Cu neighbours	Fe neighbours
α Fe K-edge RF= 0.0094	N = 9.1 δr/r = 0.0116 σ^2 = 0.0039 Å^2	N = 2.1 δr/r = - 0.0066 σ^2 = 0.0039 Å^2	none
α Cu K-edge RF=0.0021	N = 7.6 δr/r = - 0.0082 σ^2 = 0.0048 Å^2	N = 3.3 δr/r = + 0.0042 σ^2 = 0.0048 Å^2	N = 1.0 δr/r = - 0.0066 σ^2 = 0.0039 Å^2

Sample edge	Al neighbours	Cu neighbours	Fe neighbours
QC Fe K-edge RF=0.0023	N = 8.5 δr/r = - 0.0035 σ^2= 0.0039 Å^2	N = 2.7 δr/r = - 0.0157 σ^2= 0.0065 Å^2	none
QC Cu K-edge RF=0.0024	N = 8.1 δr/r = - 0.0230 σ^2 = 0.0034	N = 2.6 δr/r = - 0.0064 σ^2 = 0.0053	N = 1.3 δr/r = - 0.0157 σ^2= 0.0065

Table 2: Average environment of Cu and Fe atoms deduced from EXAFS analysis in the α-$Al_{55}Si_7Cu_{25.5}Fe_{12.5}$ and QC-$Al_{62}Cu_{25.5}Fe_{12.5}$ phases. N is the average number of neighbours of a given kind around Fe or Cu. δr/r is the relative variation of the distances with respect to those calculated from the crystallographic data of Ref. [5] for the α phase. σ^2 is the relative mean displacement for a pair. RF is the goodness of the fit.

Figure captions

Fig. 1: Modulus and imaginary part of the Fourier transform of the EXAFS oscillations $k^2\chi(k)$ at T = 15 K at the Cu K-edge.

Fig. 2: Modulus and imaginary part of the Fourier transform of the EXAFS oscillations $k^2\chi(k)$ at T = 15 K at the Fe and Cu K-edges: comparison of experimental data (symbols) and best fits (thick solid lines). The contributions of a given kind of neighbours (modulus only) around a given absorbing atom (Fe or Cu) are also shown.

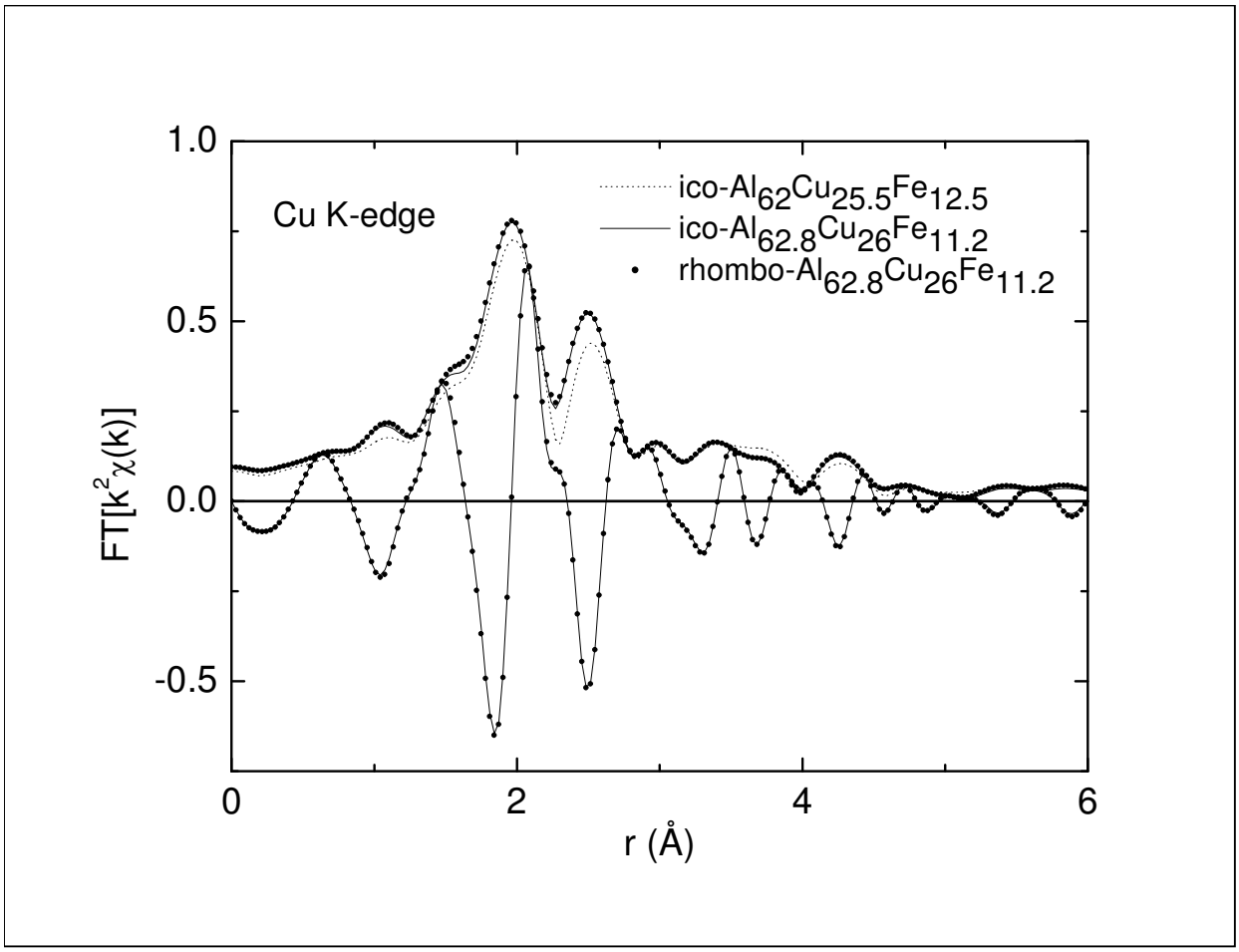

Cu K-edge
ico-Al62Cu25.5Fe12.5
ico-Al62.8Cu26Fe11.2
rhombo-Al62.8Cu26Fe11.2
FT[k2χ(k)]
r (Å)
1.0
0.5
0.0
-0.5
0
2
4
6

Fig.1

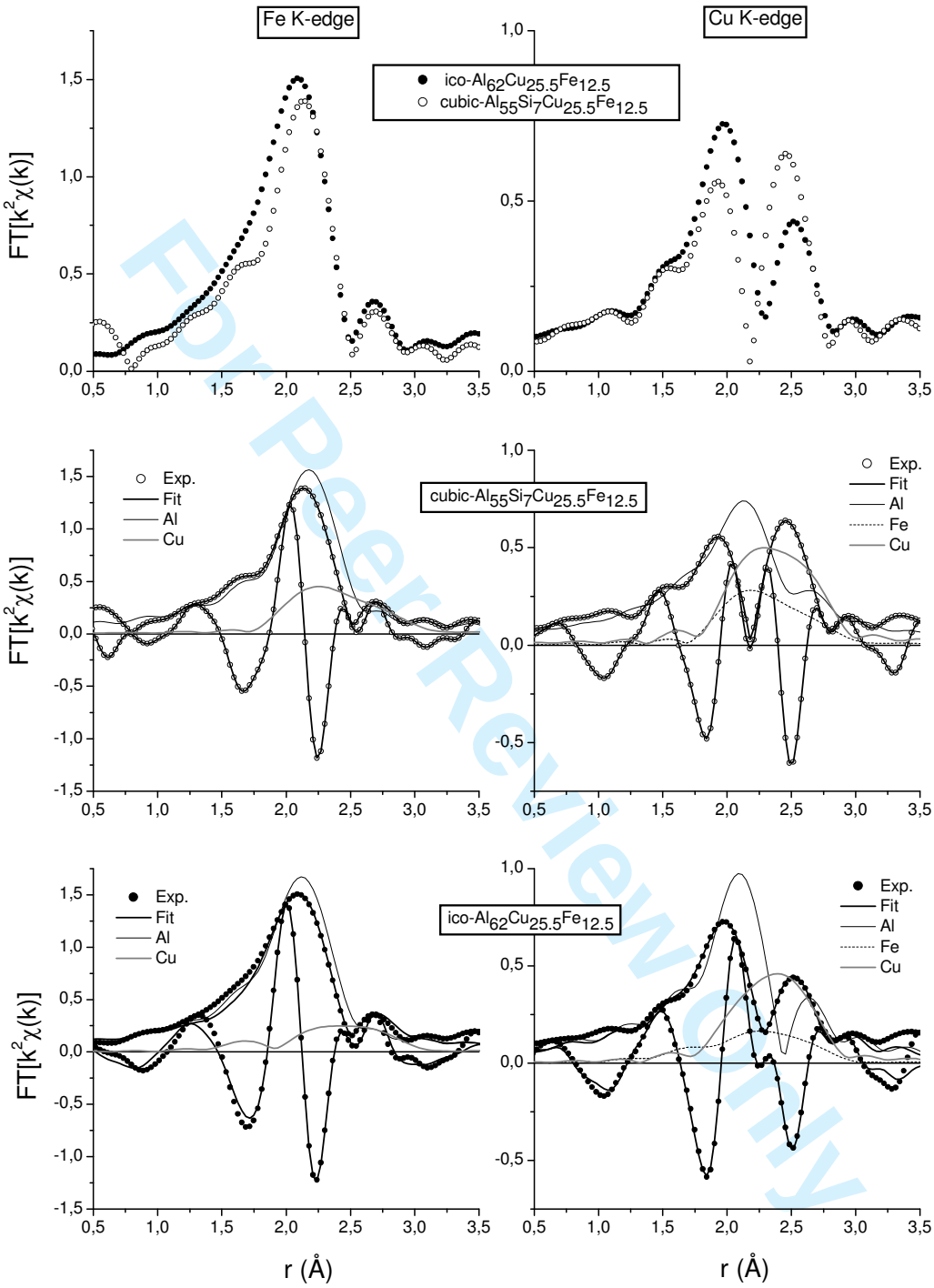
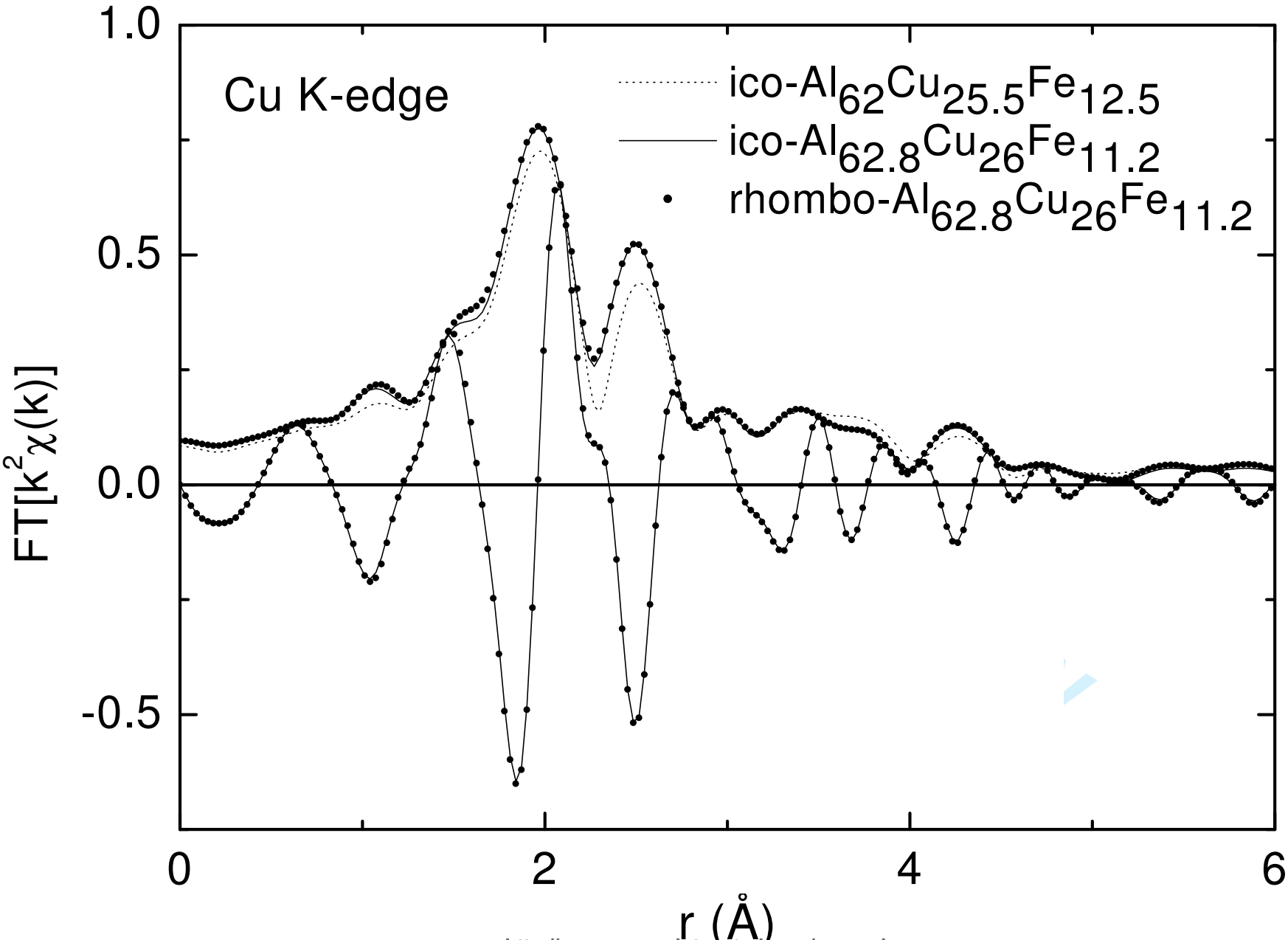


Fig. 2


Cu K-edge
ico-Al62Cu25.5Fe12.5
ico-Al62.8Cu26Fe11.2
rhombo-Al62.8Cu26Fe11.2
FT[k2χ(k)]
r (Å)
1.0
0.5
0.0
-0.5
0
2
4
6